

# **Project: LOW PLATINUM LOADING CATALYSTS**

**Principal Investigator: Radoslav Adzic**

**Research Associates: Kotaro Sasaki, Tao Huang**

**With contributions from Jia Wang, Miomir Vukmirovic  
and Junliang Zhang (student SUSB)**

**Materials Science Department,  
Brookhaven National Laboratory, Upton, NY 11973-5000**

**(This presentation does not contain any proprietary or confidential information.)**

**Philadelphia, May 24-27, 2004**

# OBJECTIVES

---

To assist the DOE in developing of fuel cell technologies by providing low-platinum-loading electrocatalysts.

- To demonstrate the possibility of synthesizing novel electrocatalysts for O<sub>2</sub> reduction with a monolayer level Pt loadings.
- To further characterize of the PtRu<sub>20</sub> electrocatalyst for H<sub>2</sub>/CO oxidation and long term tests.
- To gain understanding of the activity of Pt monolayer and the PtRu<sub>20</sub> electrocatalysts.

# PROJECT SAFETY

---

- All the work on this project is performed within the controls identified in the Experimental Safety Review (ESR) Form for this Project.
- Personnel have all the training identified by ESR.
- CO sensor installed at the CO tolerance experiment. Hazard evaluation of this experiment was performed.
- For the work at synchrotron, the safety procedures and the training requirements of NSLS are followed.

## BUDGET

TOTAL FUNDING FOR THE PROJECT (FY 02-04): \$624.000

FUNDING IN FY 04: \$250.000

# TECHNICAL BARRIERS AND TARGETS

---

## The DOE's Technical Targets for Fuel Cell Stack Systems Operating on Hydrogen (Gasoline Reformate)

year		2003	2005	2010
precious metal loading	g/kW	<2.0	0.6	0.2
durability	hours	>2000	>2000	>5000
CO tolerance (2% air bleed)	ppm	50	500	1000

# APPROACH

---

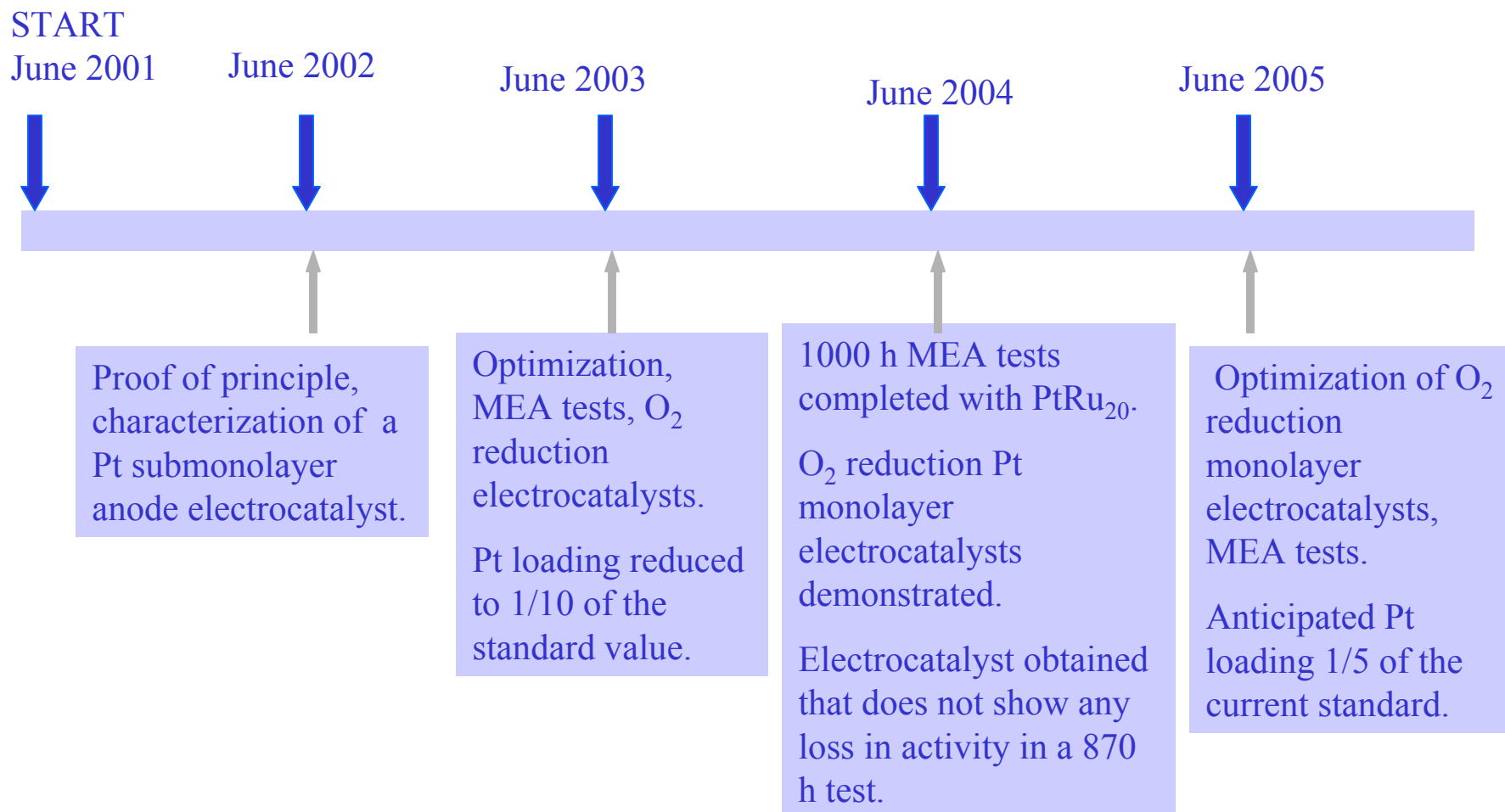
**Development of low-Pt-loading electrocatalysts by placing a submonolayer-to-monolayer of Pt on nanoparticles of suitable metals or alloys to obtain electrocatalysts with the following characteristics:**

- ultimately reduced Pt loading
- enhanced activity of Pt
- complete utilization of Pt

**Two methods for Pt monolayer deposition were developed:**

1. Electroless (spontaneous ) Pt deposition on Ru.
2. Pt deposition by replacing a UPD metal adlayer.

# PROJECT TIMELINE



## ANODE

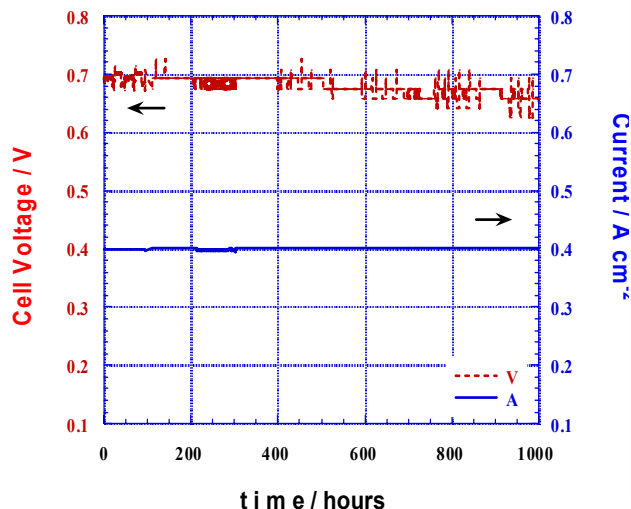
- Stability tests at LANL (F. Uribe) show **no loss of voltage after 870 h** for the PtRu<sub>20</sub> electrocatalyst with 18 µg Pt/cm<sup>2</sup> (20% Ru; 2% Pt, 3% air bleed), and small losses after 1000 h with 18 µg Pt/cm<sup>2</sup> (10% Ru; 1% Pt, 4% air-bleed) and very small losses in a 600 h test with 19 µg Pt/cm<sup>2</sup> (2% air-bleed) of combined CO/H<sub>2</sub> and H<sub>2</sub> operation.
- The DOE durability target of 2000h for 2005 can be reached with this electrocatalyst.
- The DOE target for 2005 for noble metals of 0.6 g/kW (0.3 g/kW for anode) is met for Pt: **only 0.063 g Pt/kW is necessary**. If Ru is counted, 0.630 g total metal is needed.

## CATHODE

- A Pt monolayer on C-supported metal or metal alloy nanoparticles can be an active catalyst for O<sub>2</sub> reduction.
- The Pt mass-specific activity of Pt/Pd/C is 5-8 times higher than that of Pt(10%)/C. The (Pt + Pd) mass activity is 2.5 times higher. Fuel cell tests (F. Uribe) are quite promising.
- A PdCo/C electrocatalyst was synthesized. Its activity is comparable to that of Pt.
- A Pt/AuNi/C electrocatalyst was synthesized whose activity is similar to that of Pt.

# LONG-TERM FUEL CELL TESTS AT LANL (F. Uribe)

17  $\mu\text{g Pt/cm}^2$  (10% Ru; 1% Pt)



Voltage losses after 1000 hr:

- \* with neat  $\text{H}_2$ : 40 mV
- with  $\text{H}_2 + \text{CO} + 4\%$  air: 60 mV

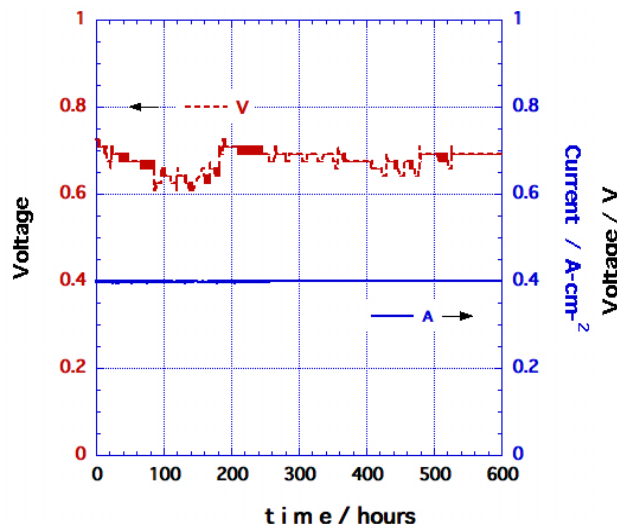
Cell =  $50 \text{ cm}^2$ ;  $T = 80 \text{ C}$ ;

A:  $0.19 \text{ mg/cm}^2$  (10% Ru, 1% Pt) C:

$0.23 \text{ mg Pt/cm}^2$  (20% Pt/C, ETEK)

Total run time = 1000 hours at constant current. 710 hours of operation with clean  $\text{H}_2$  and 290 hours with  $\text{H}_2 + 50 \text{ ppm CO} + 4\%$  air bleed.

19  $\mu\text{g Pt/cm}^2$  (10% Ru; 1% Pt)



Voltage losses after 600 hr:

- \* with neat  $\text{H}_2$ : 20 mV (0.71-0.69 V)
- \* with  $\text{H}_2 + \text{CO} + 2\%$  air: 20 mV (0.66-0.64 V)

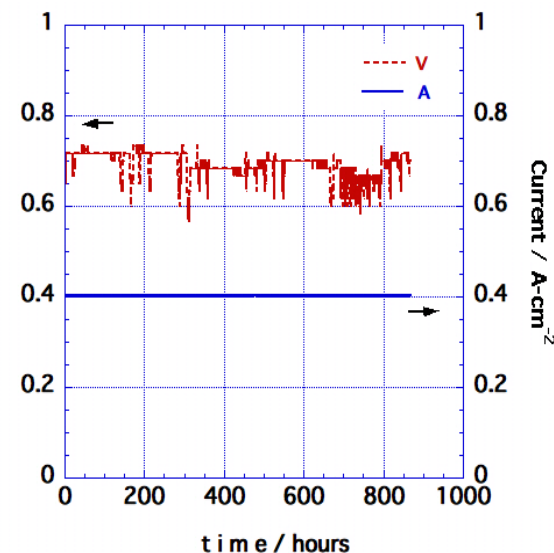
Cell  $50 \text{ cm}^2$  cell /  $T = 80 \text{ C}$

A:  $0.19 \text{ mg BNL/cm}^2$  (10% Ru; 1% Pt)

C:  $0.22 \text{ mg Pt/cm}^2$  (ETEK)

$\text{H}_2$  471 hr;  $\text{H}_2 + \text{CO}$  50 ppm +2% air bleed, 129 hr

18  $\mu\text{g Pt/cm}^2$  (20% Ru; 2% Pt)



No voltage losses after 868 hr:

- |  | initial V | final V |
|--|-----------|---------|
| * with $\text{H}_2$ :                      | 0.717     | 0.717   |
| * with $\text{H}_2 + \text{CO} + 3\%$ air: | 0.697     | 0.701   |

Cell  $50 \text{ cm}^2$  cell /  $T = 80 \text{ C}$

A:  $0.20 \text{ mg BNL/cm}^2$  (20% Ru; 2% Pt)

C:  $0.24 \text{ mg Pt/cm}^2$  (ETEK)

Running Mode: 20 A current

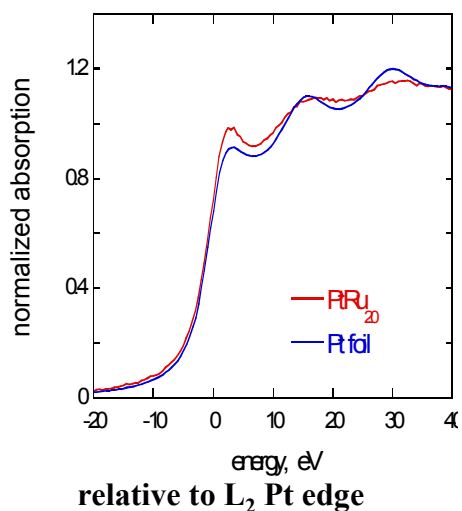
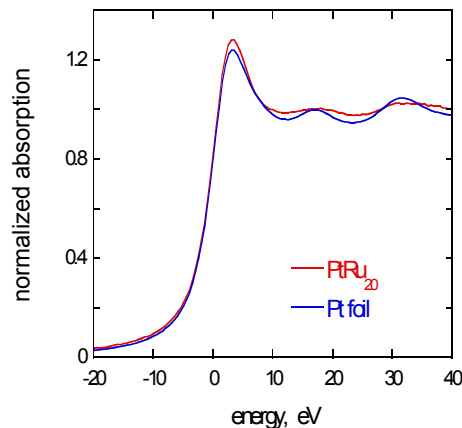
a)  $\text{H}_2$  at @ 1.3 stoich

b)  $\text{H}_2$  at @ 1.3 stoich + CO 50 ppm +3% air bleed

Air flow: constant @ 2100 sccm

In addition to CO tolerance, **the very strong surface segregation** of Pt is a key factor in its stability.

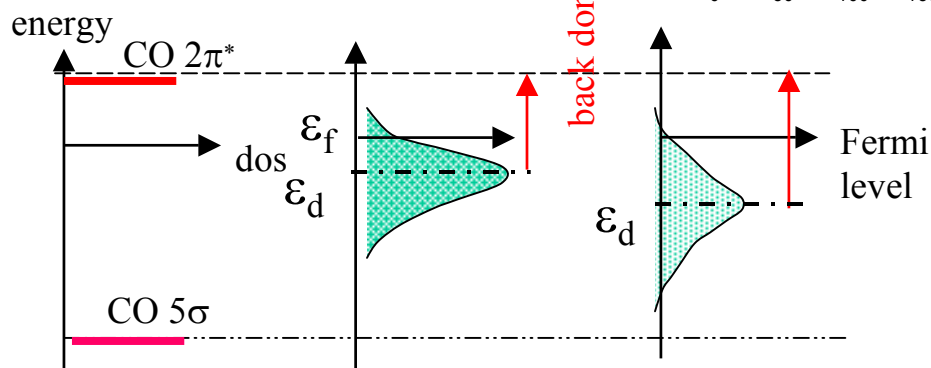
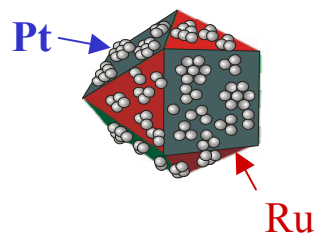
# ELECTRONIC EFFECTS vs. BIFUNCTIONAL MECHANISM IN CO TOLERANCE OF THE PtRu<sub>20</sub> ELECTROCATALYST



d band vacancy

PtRu<sub>20</sub> 0.345 (0.41V)

Pt foil 0.30



CO

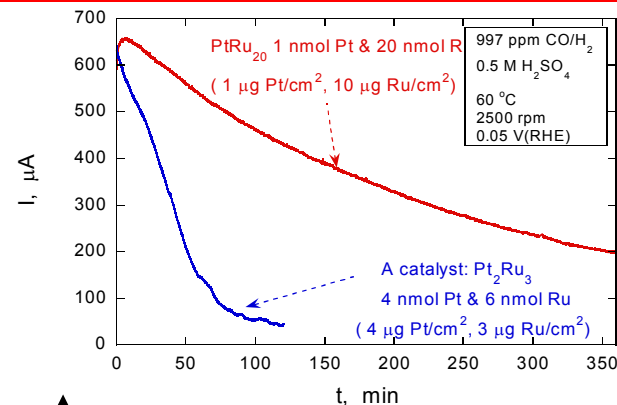
- σ electron from CO to Pt
- Back donation of Pt d electron to CO 2π\*

Pt

Strong CO adsorption

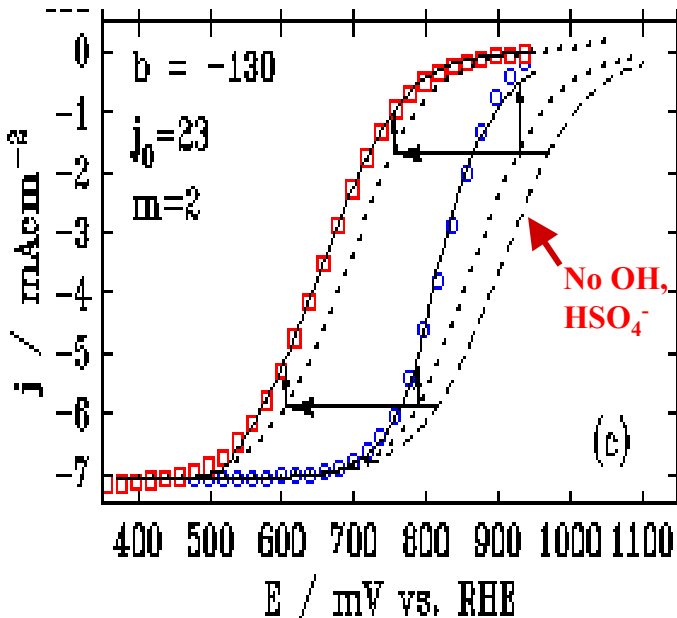
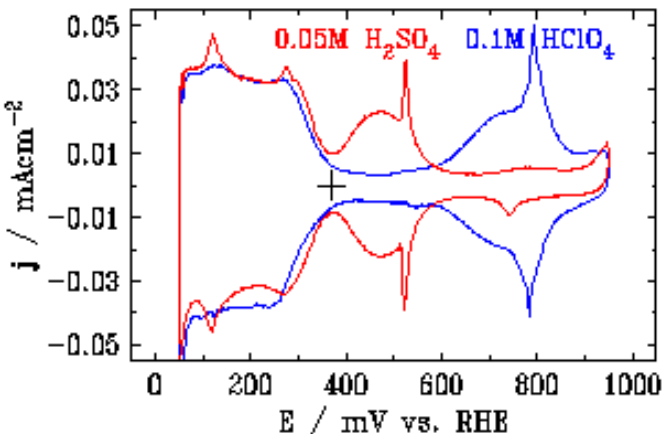
PtRu<sub>20</sub>

- Lower d-electron density
- Lower d-band center ε<sub>d</sub> (Nørskov's model)
- Back donation decreases
- Weaker CO adsorption



Conclusion: Both the electronic effects and the “bifunctional” mechanism are operative for this electrocatalyst.

# INHIBITION OF O<sub>2</sub> REDUCTION ON Pt BY ANION ADSORPTION



The kinetic currents are calculated as a function of  $E$  and the anion adsorption isotherm,  $\theta_A(E)$  using

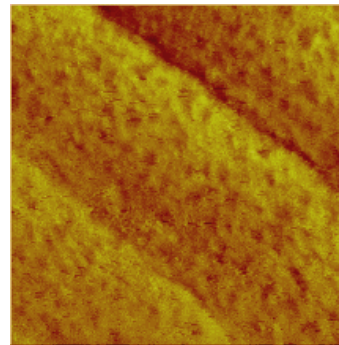
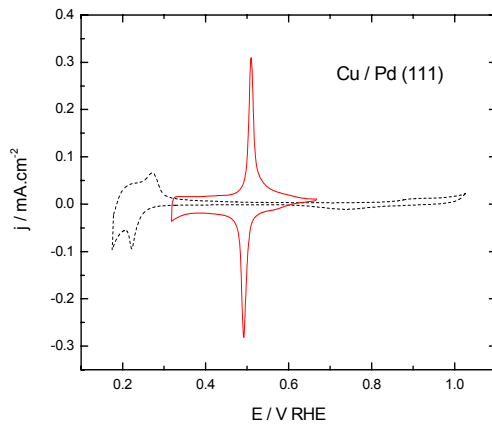
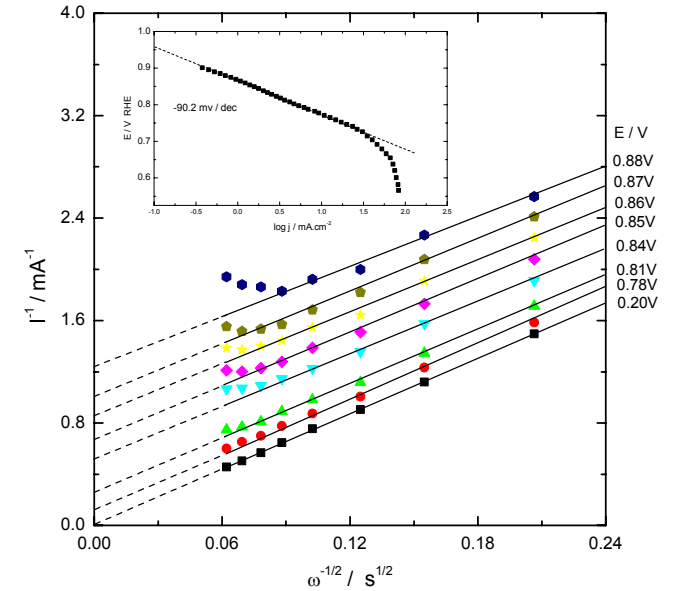
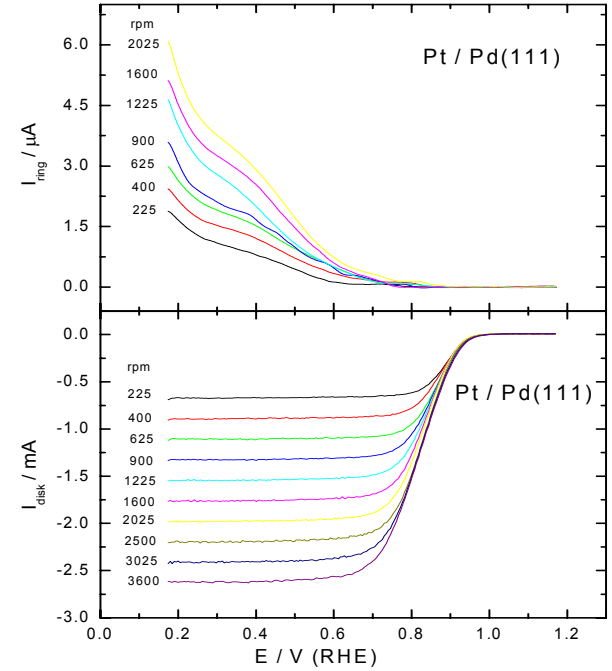
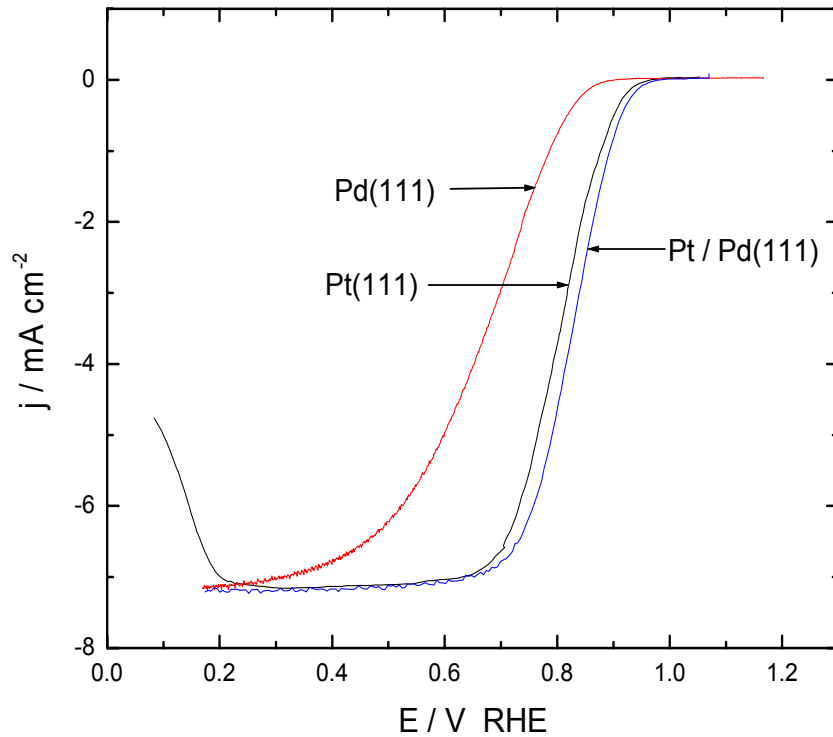
$$j_k(E) = -j_0 (1 - \gamma_A \theta_A(E))^m \exp(-2.3(E - E^0 - \epsilon_A \theta_A(E))/b),$$

where  $j_0$  and  $b$  are the **intrinsic kinetic parameters**,  $\gamma_A$  is the **geometric blocking factor**, and  $\epsilon_A$  is the **electronic effect** of adsorbed anions.

- The best fits yielded the intrinsic Tafel slope in the range  $-118$  to  $-130$  mV/dec.
- In addition to site blocking, both OH and bisulfate have a negative electronic effect on ORR kinetics, with the effect of the latter being much stronger.
- The deviation of the apparent Tafel slope in HClO<sub>4</sub> from its intrinsic value can be fully accounted for by the site blocking and electronic effects of adsorbed OH ions, which vary with coverage over the mixed kinetic-diffusion controlled region.

Wang et al. J. Phys. Chem., in press.

# O<sub>2</sub> REDUCTION ON Pt<sub>1ML</sub>/Pd(111)

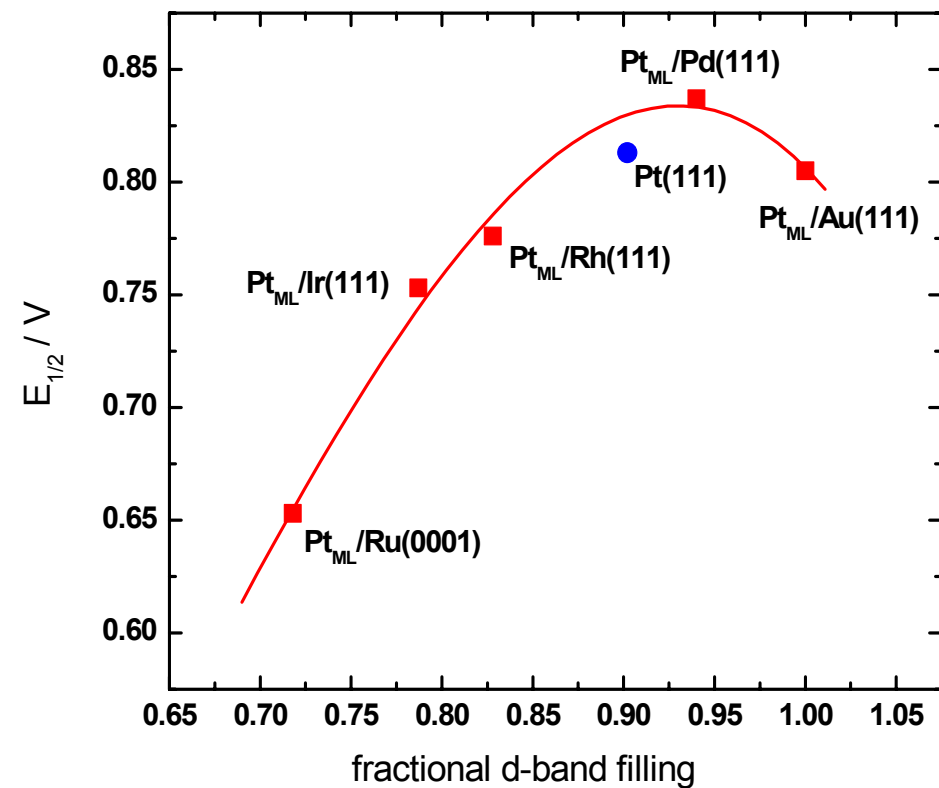


Pt<sub>ML</sub>/Pd(111)

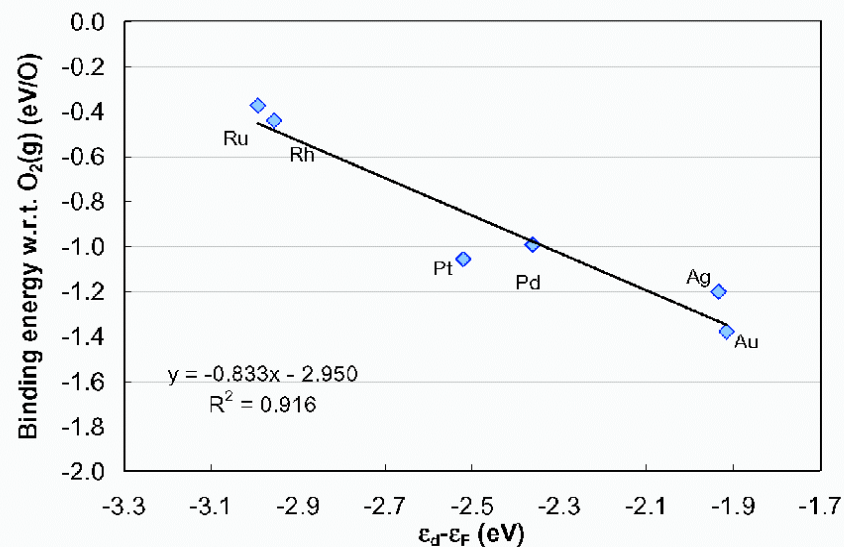
250 nm  
x  
250 nm

The reduced coverage of PtOH appears to be the cause of enhanced activity.

# ACTIVITY OF Pt MONOLAYERS AS A FUNCTION OF THE FRACTIONAL FILLING OF THE d-BAND OF SUBSTRATES



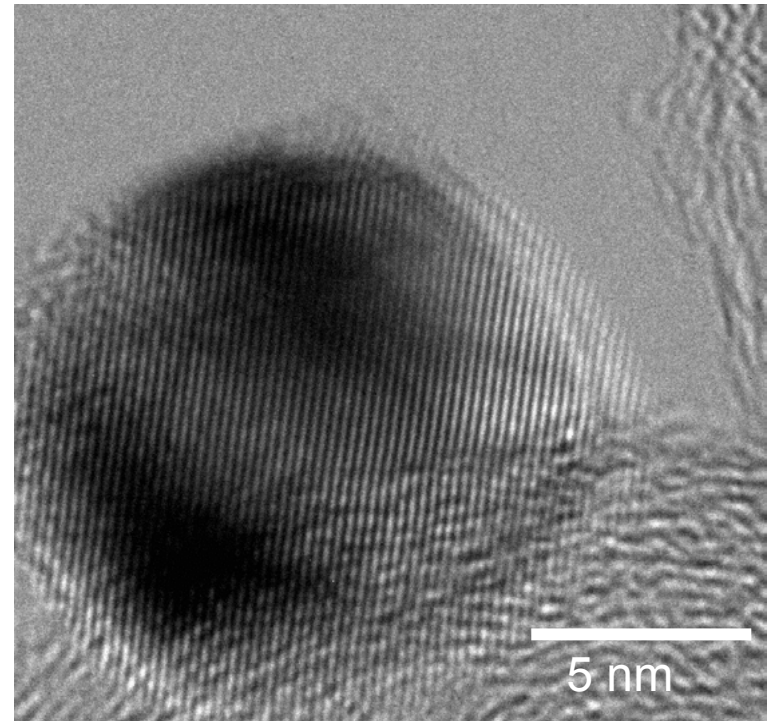
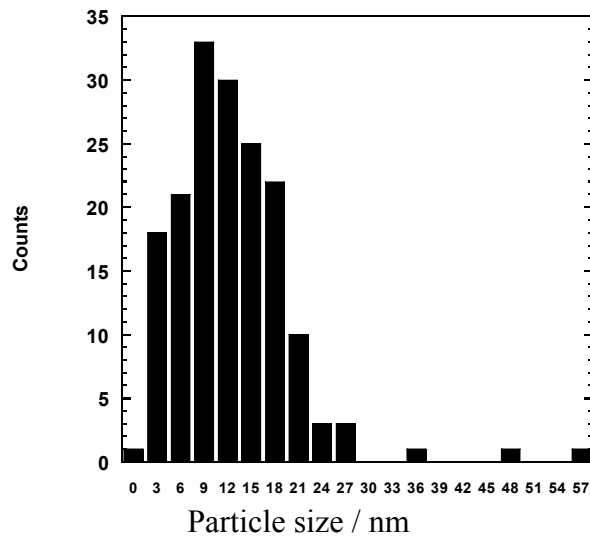
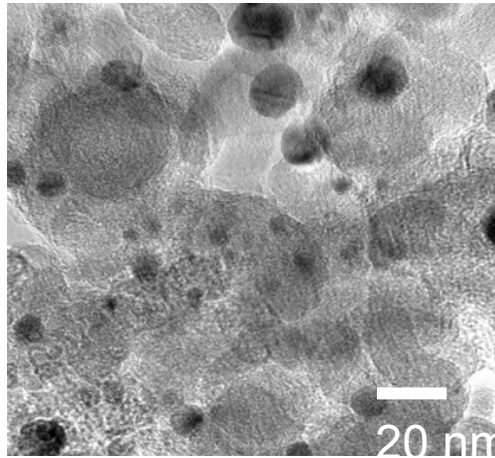
**Adsorption energies of atomic oxygen on Pt monolayers vs. d-band centers**  
fcc(111); (2x2x4) unit cell; top two layers relaxed; PW91 functional



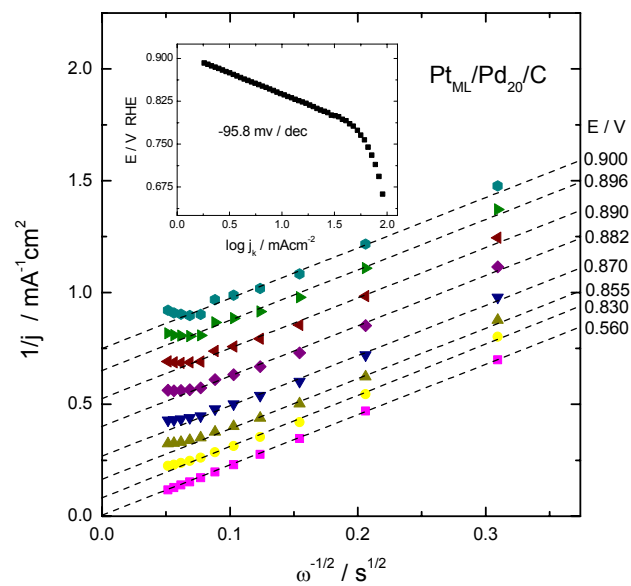
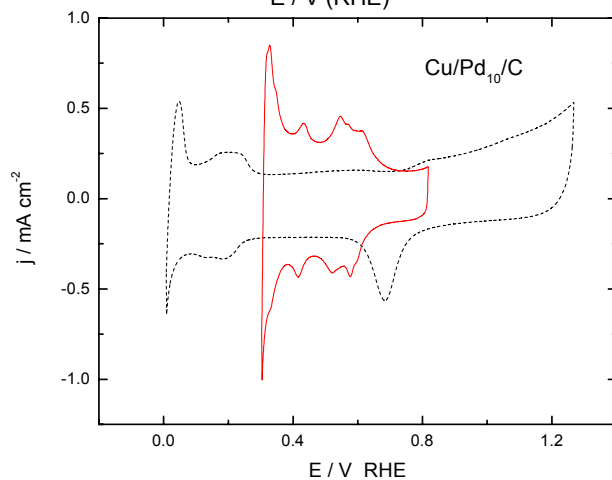
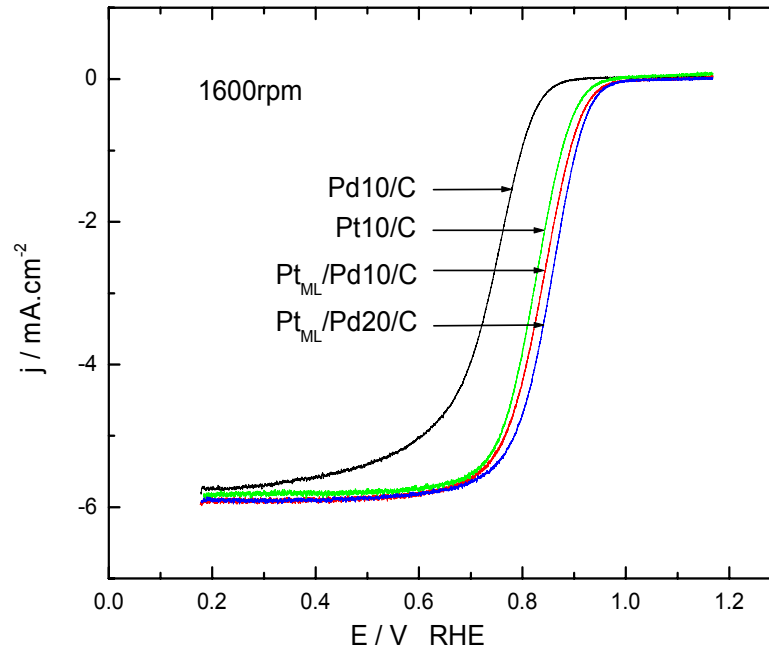
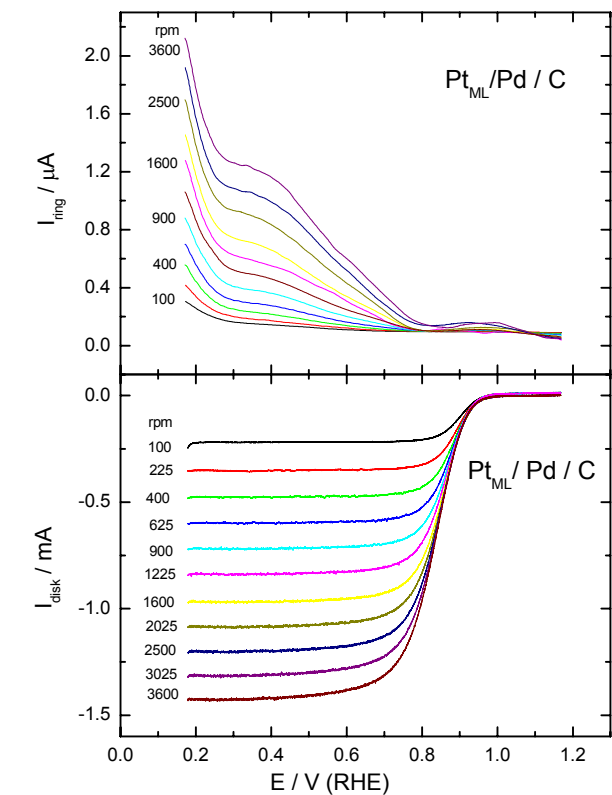
DFT calculations by M. Mavrikakis, U. Wisconsin.

# HRTEM OF Pd NANOPARTICLES ON C

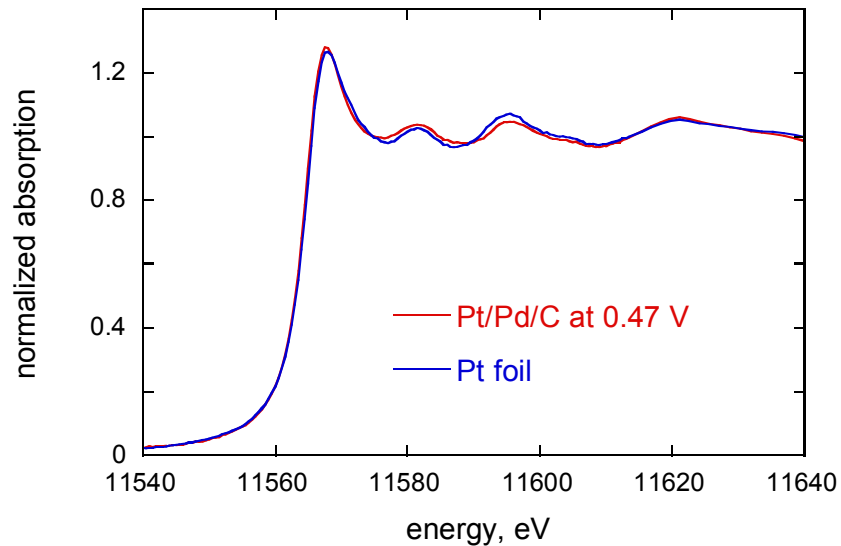
## Pd(10%) / Vulcan XC-72 commercial



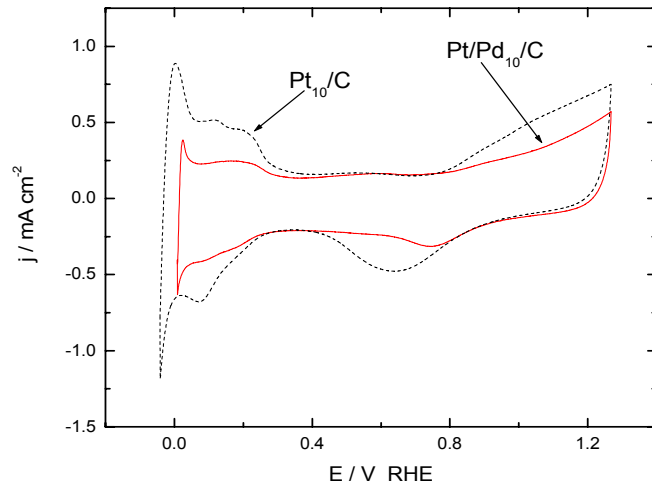
# O<sub>2</sub> REDUCTION ON Pt/Pd/C



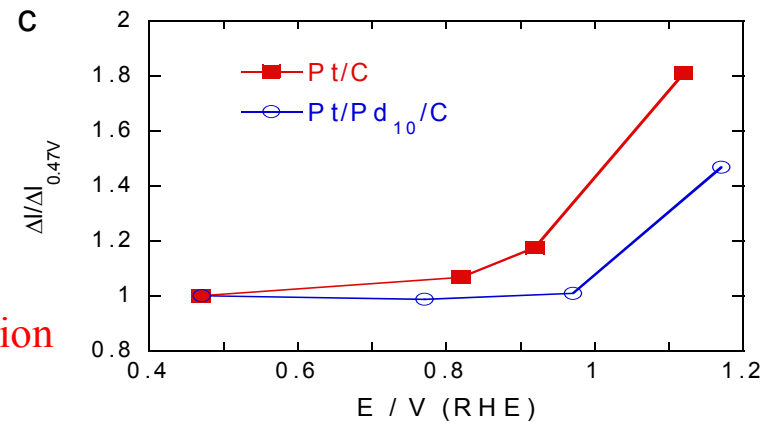
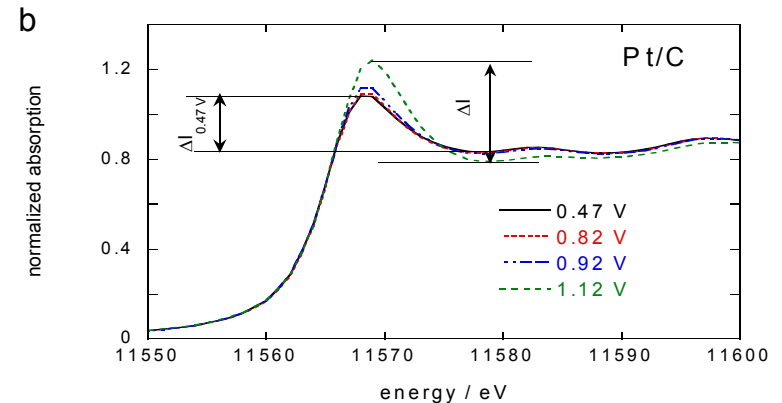
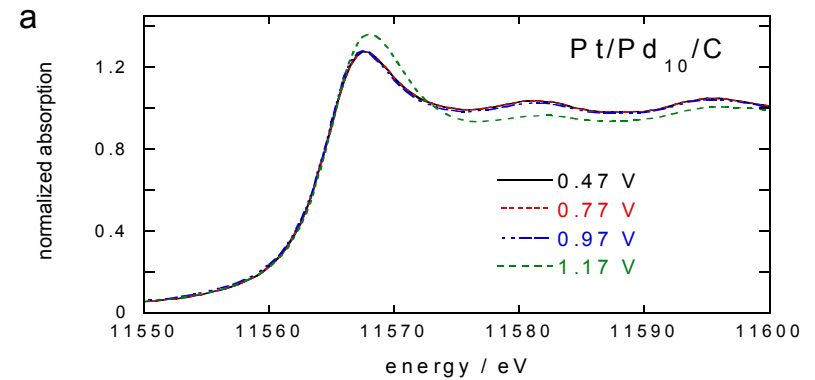
# IN SITU XANES MEASUREMENTS WITH Pt/Pd/C



XANES reveals a small change in the Pt d band.

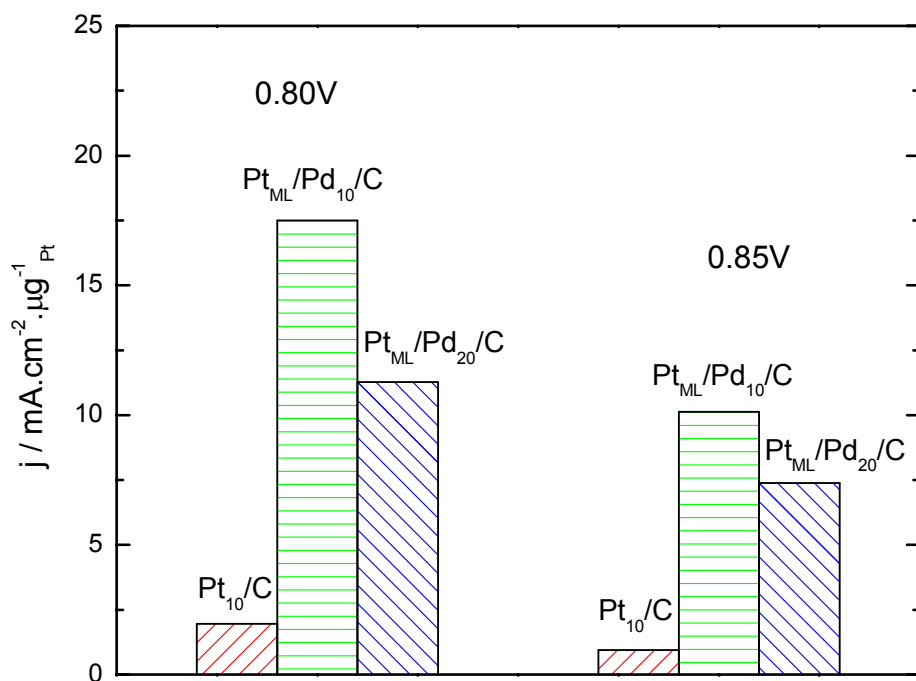


Voltammetry and XANES show delayed Pt oxidation at high potentials in comparison with Pt/C.

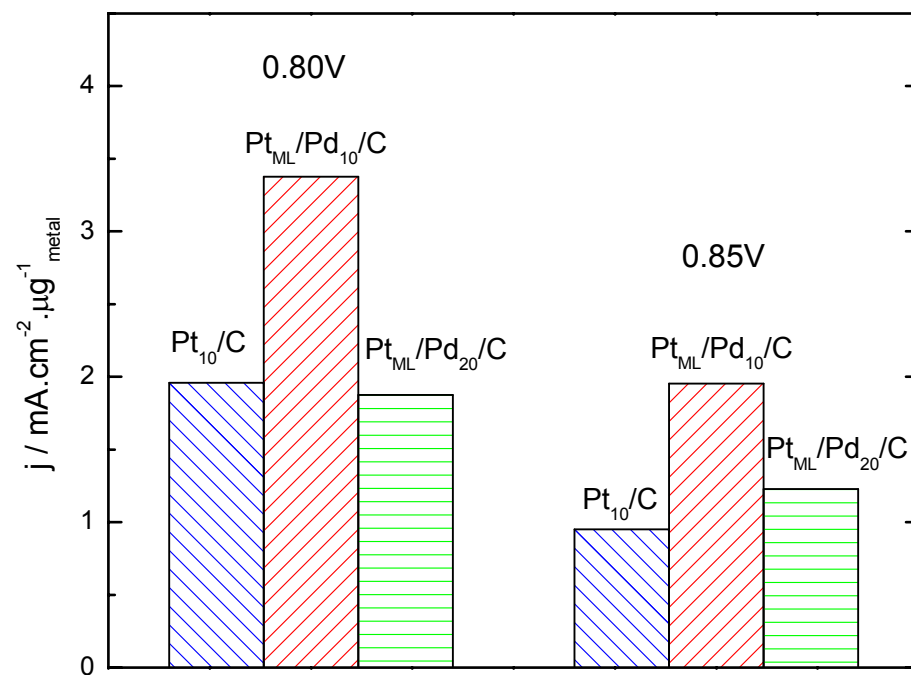


# Pt and (Pt + Pd) MASS-SPECIFIC ACTIVITY OF Pt<sub>ML</sub>/Pd/C FOR O<sub>2</sub> REDUCTION

Pt

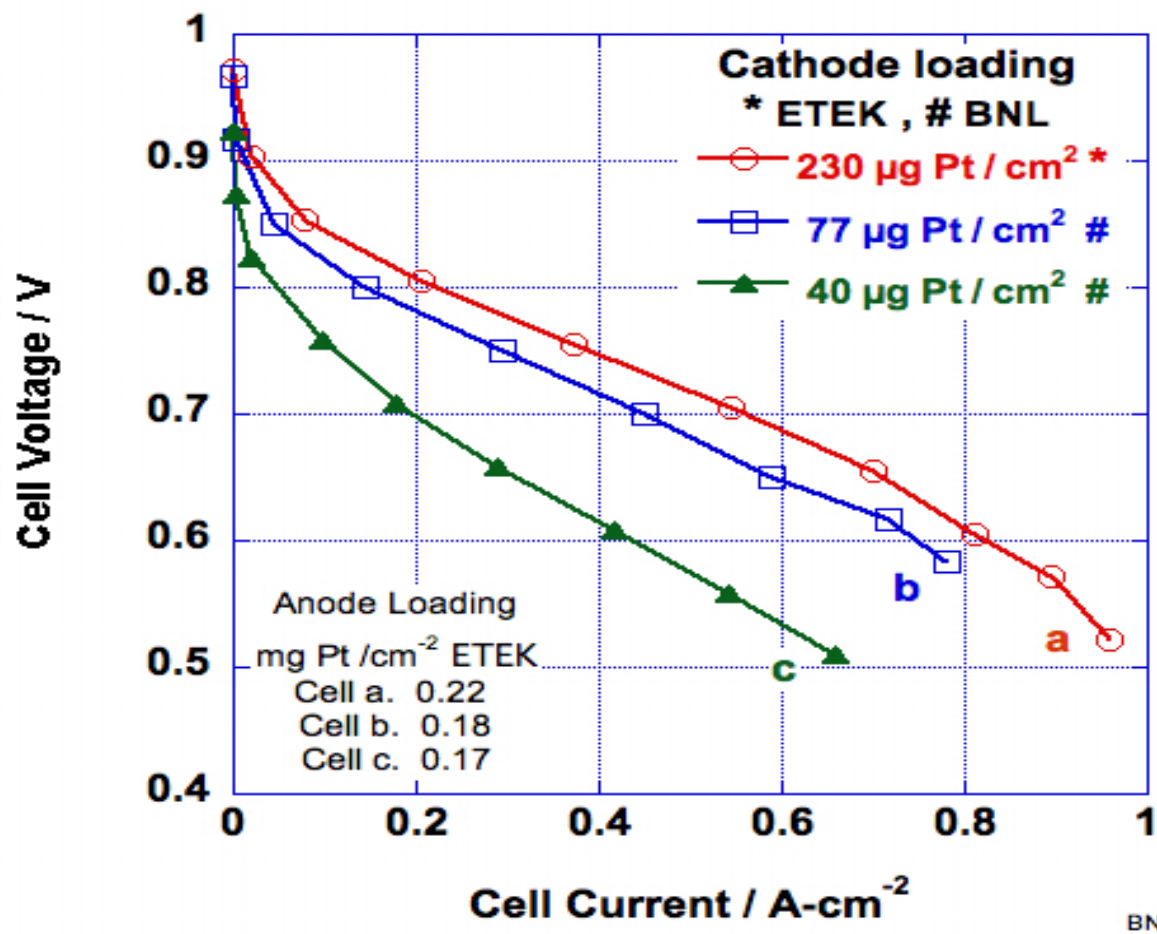


Pt + Pd



# FUEL CELL TESTS OF Pt/Pd/C AT LANL (F. Uribe)

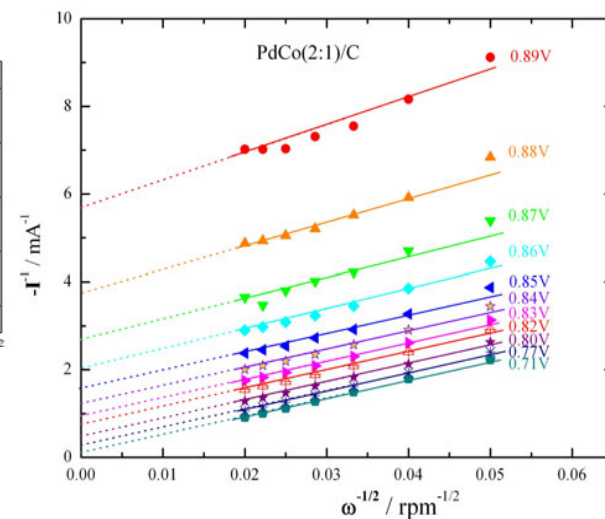
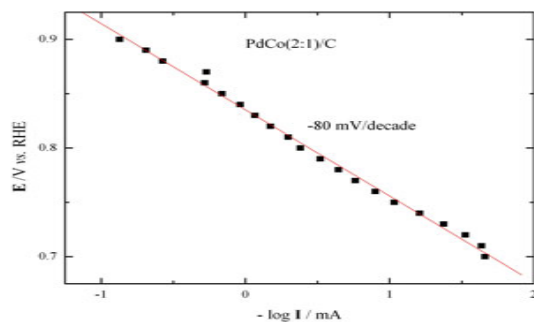
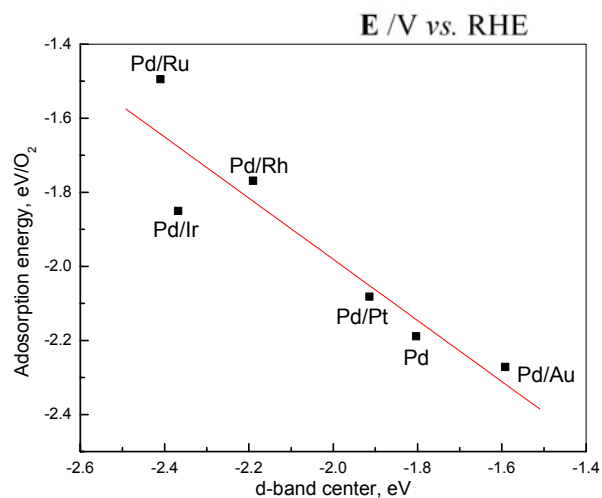
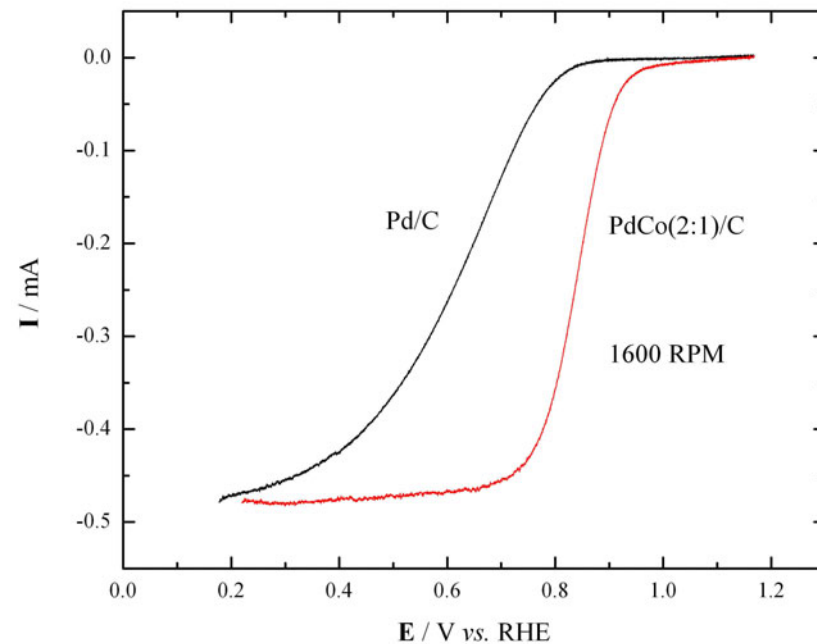
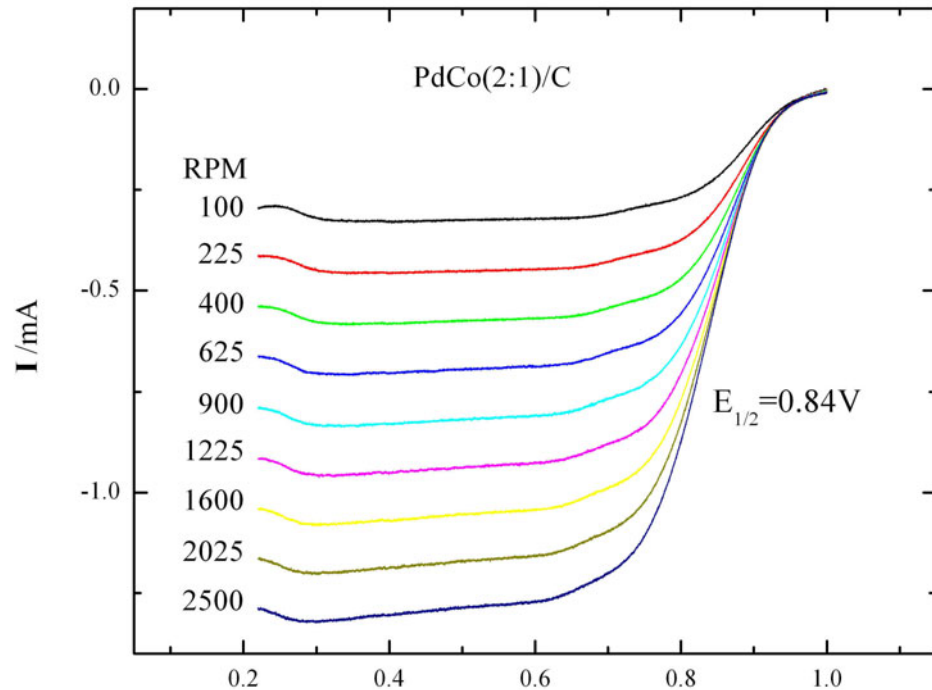
Performance of Pt-Pd/C (BNL) cathode catalyst at 80 °C.



Performance of Pt-Pd/C (4% Pt-20% Pd) cathode catalyst at 80 °C. Membrane: Nafion® N1135.

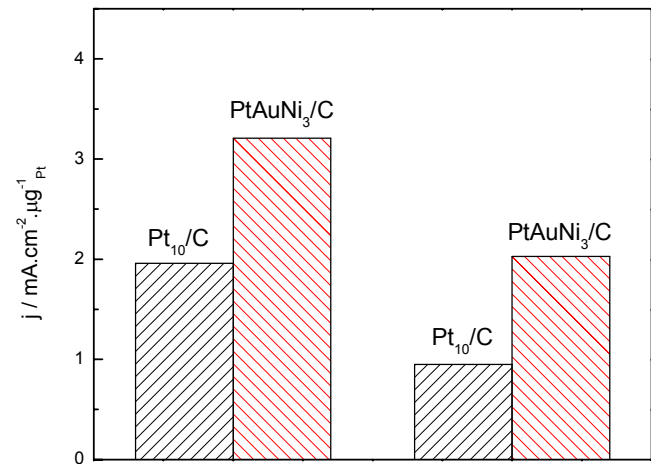
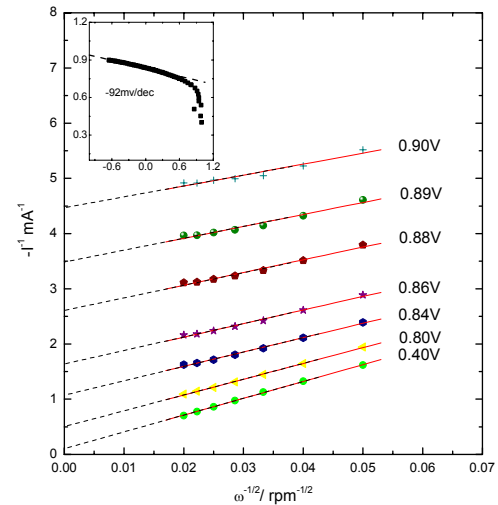
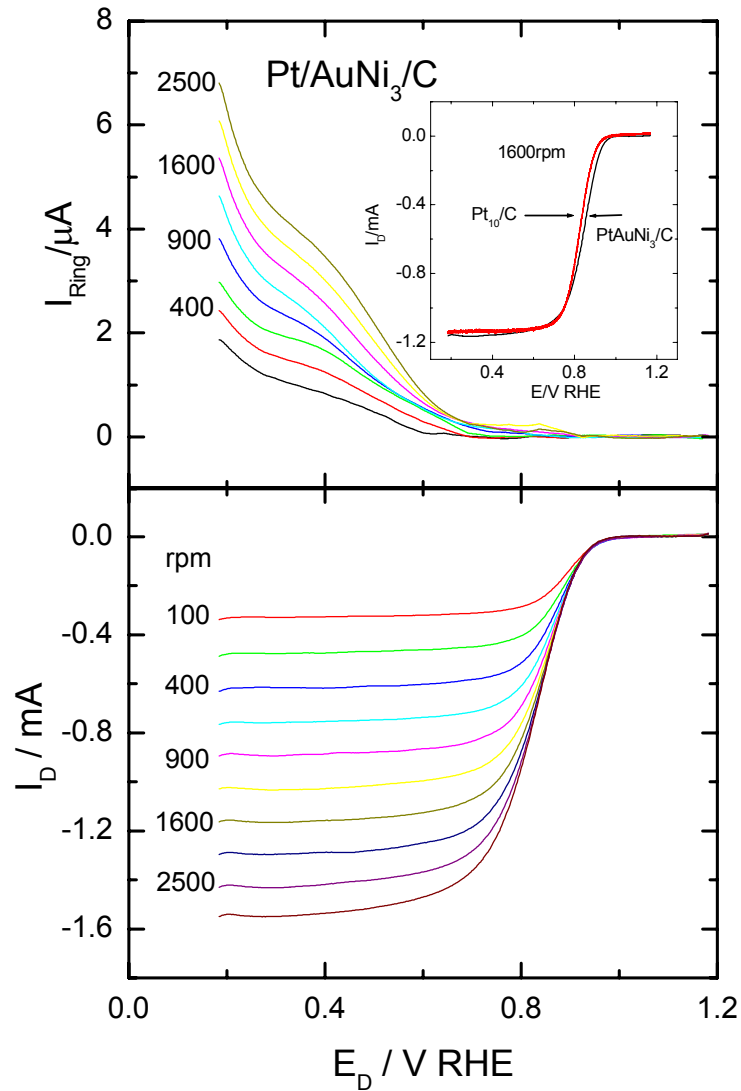
Anode loadings in mg Pt/cm<sup>2</sup>: Cell **a**: 0.22 ; Cell **b**: 0.18 ; Cell **c**: 0.17.

# O<sub>2</sub> REDUCTION ON PdCo/C



DFT calculation by P. Liu, BNL

# O<sub>2</sub> REDUCTION ON Pt/AuNi<sub>3</sub>/C



Further reduction of Au and the use of an immiscible Au<sub>ML</sub>Ni alloy seem possible.

# INTERACTIONS AND COLLABORATIONS

1. Los Alamos National Laboratory Dr. Francisco Uribe – long-term fuel cell tests of electrocatalysts.
2. Plug Power, visit, discussions.
3. Interest expressed in the  $\text{PtRu}_{20}$  electrocatalyst and collaboration.

## Publications from collaborations:

K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, Ultra-low Platinum Content Fuel Cell Anode Electrocatalyst with a Long-term Performance Stability, *Electrochim. Acta*, in press.

K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adzic, Pt submonolayers on metal nanoparticles – novel electrocatalysts for  $\text{H}_2$  oxidation and  $\text{O}_2$  Reduction, *Electrochim. Acta*, 48 (2003) 3841.

J.X. Wang, N.M. Markovic, R.R. Adzic, Kinetic Analysis of  $\text{O}_2$  reduction on Pt(111) in Acid Solutions: Intrinsic Kinetic Parameters and Anion Adsorption Effects, *J. Phys. Chem.* in press.

# Responses to Previous Year Reviewers' Comments

---

Q. Distinction from Wieckowski's catalyst not clear.

A. His: Ru on Pt for methanol oxidation; ours: Pt on Ru for H<sub>2</sub>/CO oxidation.

Q. Not clear how structure/phase behavior (of CO) is exploited to design practical catalysts.

A. Knowing adsorbate's mobility, lateral interactions and adsorption sites can help in designing electrocatalysts.

Q. Cathode materials of higher importance and needs to be expanded.

A. The work on cathode materials has been expanded.

# FUTURE WORK

## H<sub>2</sub> oxidation

1. Pt submonolayers on non-noble metal alloy nanoparticles.

## O<sub>2</sub> reduction

1. Further development of a Pt/Pd/C electrocatalyst. Tests at LANL.
2. Further development of immiscible Au-non-noble metal alloy nanoparticles as support for Pt.
3. Multi-metal monolayers to reduce PtOH coverage and to modify the electronic properties of Pt.
4. Non-noble metal alloys as support for Pt.

